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An overview of ionic liquids as solvents in biodiesel synthesis

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ABSTRACT

Transesterification is the most common method for producing biodiesel. Known as a suitable substitute to diesel fuel, the synthesis involves renewable sources as feedstock. Application of both organic and inorganic solvents in biodiesel production has been widely established. However, as the properties of conventional solvents are perpetually hazardous to human and environment, utilization of greener alternative is a better option. Among the various types of solvents available, ionic liquid seems prevalent. An ionic liquid is a combination of cations and anions, has low or negligible vapor pressure, and exists as liquid at temperature below 100 °C. The prospect of ionic liquids as green solvents in chemical processes is increasing in recent years, especially in biodiesel synthesis. This paper highlighted the properties of ionic liquids that emphasized their versatility as solvents, and the use of switchable ionic liquids as green solvents is also presented. The roles of ionic liquids in biodiesel synthesis are discussed, focusing on their pertinent capability as solvents, particularly as catalysts for transesterification reaction. Since the cost of ionic liquid may be an issue, a brief discussion about the recyclability of ionic liquids is also included.

Contents

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1. Introduction

Energy crisis seems to be inevitable as the global demand for energy keeps rising as a consequence of industrial development and population growth worldwide [1]. Increased oil consumption in daily activities raised the alarm among consumers as we are dependent on crude oil and its derivatives. If the trend continues in coming years, there might be a possibility that in the future, there will be no more crude oil as there are finite amount of resources. This unfeasible situation can lead to shortage of crude oil as the energy demand escalates, and indirectly raised the price of crude oil [2]. Other than the possibility of diminishing fossil fuel reserves, the detrimental effect of exhaust gases from petroleum-based fuels on the environment is also worrying. Combustion of these fuels releases harmful and hazardous substances into the atmosphere. The biggest concern about the product from engine combustion is carbon dioxide, as it is one of the primary greenhouse gases in the Earth's atmosphere to contribute to global warming [3]. As more and more carbon dioxide is produced and confined in the atmosphere, the sun's heat is also trapped and increased the Earth's surface temperature, resulting in the rise of sea level due to the melting of ice sheets [4].

The limited crude oil reserves and environmental-threat exhaust gases have reiterated the importance of crude oil substitute. Biodiesel has potentials as an alternative to petroleum diesel. Biodiesel can be produced via chemical reaction between a feedstock; either vegetable oil or animal fat, to produce methyl esters [5]. Advantages of using biodiesel compared to diesel fuel are that biodiesel is renewable, emit fewer hazardous substances from exhaust gases, and its usage also reduces the dependency on petroleum-based fuel. Emission of carbon dioxide into the atmosphere can be reduced by substituting diesel fuel with biodiesel. A study by Sheehan et al. [6] stated that using 100% pure biodiesel (B100) reduced net carbon dioxide emissions by 78.45% compared to petroleum diesel. In addition, biodiesel is said to be carbon neutral as plants absorb carbon dioxide for photosynthesis process, thus reducing the amount of carbon dioxide in the atmosphere [7].

There are several methods available to obtain biodiesel from its feedstock. These include direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification [8]. Transesterification is defined as a process where esters of saturated and unsaturated carboxylic acid (also known as triglyceride) react with alcohol in the presence of catalyst to produce mixtures of fatty acid esters as the main product and glycerol as by-product [9]. The reaction between triglycerides and alcohol to produce fatty acid esters is shown in Fig. 1. This process is mainly carried out to reduce the viscosity of the feedstock, which can sometimes have high viscosity and not suitable for direct use in diesel engine. During the process, alcohol molecules replace the glycerol backbone, thus producing alkyl esters of fatty acids. Transesterification process can be influenced by various parameters, including free fatty acids and water content, molar ratio of alcohol to oil, catalysts type and loading, reaction temperature and stirring rate [10].

Organic and inorganic solvents are commonly utilized in biodiesel synthesis as catalyst [11–13], solvents for enzyme-catalyzed transesterification [14,15], and extraction agent for extracting lipid prior to conversion into biodiesel [16,17]. Although the solvents are widely available and can be obtained with reasonable price, issues regarding volatility, toxicity, physical hazards and possibility of environmental contamination can reduce the usage of conventional solvents in the future. As the awareness about the risk of using these solvents increased, the search for their alternatives becomes a priority. One alternative is found in ionic liquids (ILs). ILs are defined as salts that are usually liquid at room temperature due to its melting temperature of below 100 °C, and are solely composed of several cations and anions. ILs are eminent and green, suitable to replace conventional solvents in chemical synthesis. Among the unique characteristics of ILs are negligible vapor pressure, good solubility in both organic and inorganic materials, able to form multiple phase systems due to their miscibility, and highly tunable for specific tasks [18].

Ionic liquids are produced through different combinations of cations and anions. Physicochemical and thermal properties of ILs are influenced by the types of ions used. Manipulation of ILs functional groups can be applied to produce task-specific ionic liquids (TSILs) for different applications. The applications include substitution to solvents of higher volatility, purification of gases, homogeneous and heterogeneous catalysis, biological reaction media, and removal of metal ions [19]. ILs are also involved in biomass pretreatment and cellulose dissolution [20]. More recently, there is an increasing tendency of using ionic liquids in biodiesel synthesis of vegetable oils and animal fats, where ILs can be used as either catalysts or solvents [21]. The purpose of this review is to highlight the prospect of ionic liquids as green solvents in biodiesel synthesis. Their properties are presented to elucidate their advantages over conventional organic and inorganic solvents. In addition, recycling and reusability of ionic liquids are also discussed.

2. Ionic liquids properties

The utilization of ionic liquid (IL) in various industrial applications has progressed since its early discovery. Experiments and researches are conducted in order to obtain a deep understanding about the wide range of potentials that they can offer. Ionic liquids have been used and applied in a variety of processes, among them as homogeneous catalyst in hydrogenation and hydroformylation reactions, in removal of heavy metal traces and aromatic hydrocarbon, in protein extraction, and alkene/paraffin separation [22]. By definition, ionic liquids are organic salts that are solely composed of ions (cations and anions) with low melting temperatures, negligible vapor pressure, and exceptional thermal and chemical stability. They are liquid at room temperature and can be produced through different combinations of cations and anions. Fig. 2 represents cations and anions commonly used to prepare ionic liquids.

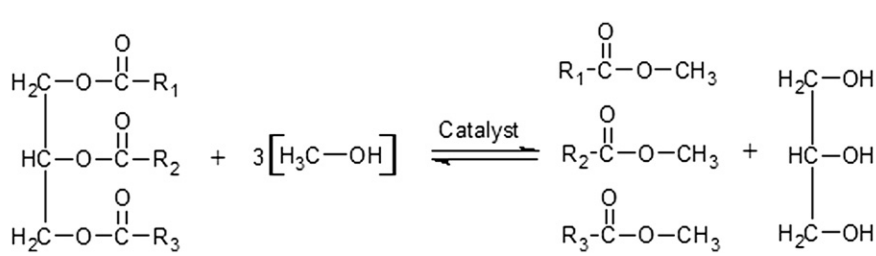


Fig. 1. Transesterification of biodiesel from triglycerides.

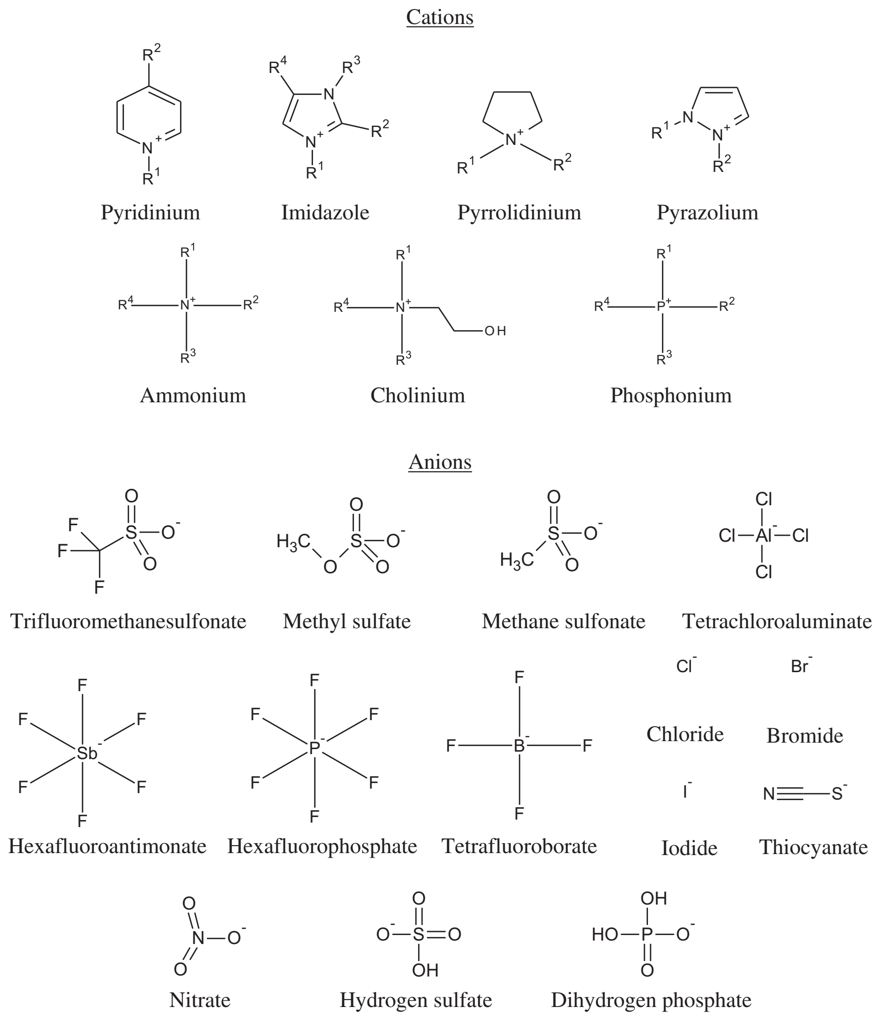


Fig. 2. Commonly used cations and anions in ionic liquids.

2.1. Negligible vapor pressure

Ionic liquids are considered as greener solvents compared to common volatile organic compounds (VOCs) as the vapor pressure is low, whereas VOCs have high vapor pressure at room temperature. The property of ILs is suitable as solvents for conducting organic synthesis. Due to the negligible vapor pressure, they generally do not evaporate or boil except at very high temperatures and can operate over a large temperature range. Many of the commonly used ionic liquids melt below room temperature and often start to decompose at elevated temperature, therefore providing options of using high temperature for conducting synthesis in chemical applications. No vapor pressure means non-volatile solvent and prevents the loss of solvent to the atmosphere, which is beneficial in terms of environment sustainability. This characteristic of ionic liquid creates a better way to remove VOCs without the loss of IL via evaporation, and also for recovery purpose. In the cyclization of 1-dodecene to cyclododecane using 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]–$AlCl_3$) as catalyst, Qiao and Deng [23] removed a more volatile component (ethanol) by heating the product of the reaction at 80–90 °C without the loss of ionic liquid during the recycling process. Due to the high thermal stability, IL remains in the liquid phase, and only ethanol is removed. Liu et al. [24] removed more volatile components from IL by using a rotary evaporator, followed by distillation under reduced pressure to recover IL, and the water was removed for preparation of the next cycle.

Aschenbrenner et al. [25] used thermogravimetric analysis (TGA) to determine the vapor pressure of ionic liquids, liquid polymers and derivatives of glycerol. Langmuir equation was applied for calculating vapor pressure of the substances used. The results were in agreement with the theory of ionic liquids having low vapor pressure, with the analysis conducted at a temperature of 120 °C for ILs. [EMIM][$EtSO_4$] recorded vapor pressure of 2.0 Pa, and the lowest was [HMIM][TfO] with 1.0 Pa. Bier and Dietrich [26] pointed out that the strength of interaction between ionic liquids particles were stronger than dispersion forces and hydrogen bonds, but weaker in comparison to Coulomb forces. Other than that, they concluded that the strong ionic bonds and low melting temperatures of ILs contributed to their extremely low vapor pressures. Although the idea of negligible vapor pressure of IL is well-established, studies showed that IL can also be distilled and vaporized for recovery purpose. A study on the volatility of ionic liquids was carried out by Earle et al. [27] using Kugelrohr apparatus. ILs were vaporized under vacuum at 200–300 °C and were then collected after condensation. Some of them decomposed under vacuum conditions, and further reduction in pressure increased the distillation rate of IL. $[NTf_2]^-$, $[OTf]^-$ and $[PF_6]^-$ anions were successfully distilled without significant decomposition in either residue or distillate. However, recovery of IL by distilling it would be energy extensive as it requires considerably high temperature. Removing more volatile components is a better option in terms of energy usage, although the purity of IL can be affected if there is an incomplete removal of other compounds.

2.2. High thermal stability

Another essential property of ionic liquids is its thermal stability. Ionic liquids commonly have higher thermal stability compared to other conventional solvents, meaning that ILs are less susceptible to decomposition at high temperature. This significant characteristic is contributed by its high thermal decomposition temperature (T_d). Thermogravimetric analysis (TGA) onset temperature is the most common method used to represent thermal stability on an IL because of the ease in measurement and reproducibility [28]. Thermal properties of ammonium- and imidazolium-based ionic liquids were studied by Ngo et al. [29], and one of them was thermal decomposition temperature using data obtained from thermogravimetric analysis and scanning differential thermal analysis (SDTA). All the studied ILs have onset temperature of more than 280 °C, with the lowest being 285 °C ([EMIM][Cl]). Their study showed that the type of pan used in the analysis influenced the decomposition temperature of ILs, and the presence of hydrogen ring affected the thermal stability of imidazolium ions.

Van Valkenburg et al. [30] investigated the thermal properties of ionic liquids, which contributed to their suitability as the heat transfer medium. Ionic liquids used in their study were 1-methyl-3-ethylimidazolium tetrafluoroborate ([EMIM][BF_4]), 1-methyl-3-butylimidazolium tetrafluoroborate ([BMIM][BF_4]), and 1, 2-dimethyl-3-propylimidazolium bis(trifluorosulfonyl)imide ([DMPI][Im]). Thermal gravimetric analyses were conducted to determine the thermal decomposition temperature for samples. They discovered that all the ionic liquids have thermal decomposition onset above 400 °C, with [DMPI][Im] which was the most stable among them. The results concluded that ionic liquids are thermally stable even at elevated temperatures due to its high decomposition temperature. Water contamination did not affect the thermal stability of the anion, and so did the addition of 10 mol% chloride contamination. Du et al. [31] investigated decomposition temperature of ILs synthesized from lactam compounds (i.e. caprolactam and butryolactam). By using the TGA method, the results illustrated decomposition temperatures ranging from 117 to 249 °C. Both cations and anions used affected the thermal stability of ILs. Caprolactam-based ILs showed higher thermal decomposition temperature with respect to the same anion.

2.3. Phase transition behavior

In general, IL is available in liquid form at temperature below 100 °C [32]. Upon cooling of ionic liquid, it can change into solid phase. This change in phase of an IL can be determined by its melting point (T_m), or glass transition temperature (T_g) [28]. In contrast to the upper temperature limit of the liquid range controlled by the thermal decomposition temperature, this lower temperature bound is important in knowing the properties at which ionic liquid changed its phase. Melting point is the temperature limit where solid turns into liquid due to the change in the structure of ions or molecules, whereas glass transition temperature occurred when the solid state changed into an amorphous solid condition [33]. In other words, IL behavior changed from hard and brittle characteristics into an elastic and flexible state. Glass transition temperature of an IL will always be lower than its melting point. Greaves et al. [34] measured phase behavior properties for a range of protic ionic liquids, including their melting point and glass transition temperatures. Differential scanning calorimetry (DSC) technique was used to perform thermal analysis. As expected, all T_g were lower than T_m, with the highest which was −44 °C (ethanolammonium methyl sulfate). For the melting point, some ILs were not in liquid form at room temperature, with diethylammonium sulfate which has the highest melting point (200 °C). The substitution of a hydroxyl group in IL has larger influence on its glass transition temperature compared to the alkyl chain length, while the melting point is affected by the packing efficiency of the crystal lattice.

The phase transition behavior of ionic liquids was studied by Crosthwaite et al. [35]. Pyridinium, imidazolium and quaternary ammonium cations were paired with different types of anions. Most ILs have glass transition temperatures, while the rest exhibit either only melting point, or both. Among the cations used, pyridinium-based ILs showed higher T_g and T_m compared to imidazolium- and ammonium-based ILs. In addition, anions used also influenced the phase transition behavior. For example, ILs with bromide anion ($[Br]^-$) have the highest T_g and T_m, while the behavior of ILs with $[Tf_2N]^-$ is in contrast to the former anion. The comparison of thermal properties between monocationic and dicationic imidazolium-based ionic liquids was reported by Shirota et al. [36]. They also used differential scanning calorimetry test to measure melting points and glass transition temperatures of ILs. Melting points increased with decreasing alkyl chain length of cation used, and are higher for dicationic ILs compared to monocationic ILs. The same trend was observed for glass transition temperatures, and increased when the following anions order was used: $[NTf_2]^-$, $[NPf_2]^-$, $[BF_4]^-$, $[NO_3]^-$. The lower temperature limit of studied ILs was somehow correlated to the behavior of cation used, with the dicationic ILs which were denser than monocationic ILs.

2.4. Solubility and miscibility with reactants

The ability of ILs to form biphasic or multiphase with reaction products enables easier separation of ILs. This ability is contributed by the solubility and miscibility of an ionic liquid, which can be tailored for specific task or process. Ionic liquid can be dissolved in both inorganic and organic compounds, depending on its solubility and miscibility. An important aspect for IL is that it should have partial or complete solubility for the reactants, but poor solubility for the reaction products. Solubility with reactants improved the reaction by allowing reactants to become in contact with each other. On the other hand, the product phase can be separated by simple decantation as it is insoluble with ionic liquid, and this allows recycling of ionic liquid. One of the factors affecting this property is the presence of ions in an IL, which are anion and cation. The anion generally controls the extent to which an IL is miscible with water, where the solubility of water in ionic liquid can be varied by changing the anion from $[Cl]^-$ to $[PF_6]^-$ [37]. Other factors that influence the miscibility of IL with water are the degree of coordination of ions in an IL and the length of the alkyl chain on cations [38]. Zhang et al. [39] adapted a simple decantation method to obtain liquid esters due to the higher degree of miscibility of the IL with water and partial immiscibility with the product ester. Besides, more products were obtained as the esterification reaction equilibrium favored the product side without the need to remove water produced during the reaction. This is due to different in miscibility of the reaction products. The esterification process was repeated after the recovery step of IL, and there was no noticeable change in the conversion and selectivity of ester even after 6 runs.

Ionic liquids can be used for dissolution of cellulose. Other than being environmental friendly solvents, the ability of ILs to dissolve cellulose is also beneficial as cellulose can be regenerated after recovery, and ILs can be recycled and reused. Furthermore, ILs have an advantage over common organic solvents for dissolving cellulose, as organic solvents are not able to break the strong inter- and intra-molecular bonds of highly crystalline nature of cellulose. Swatloski et al. [40] used different kinds of ionic liquids

for conducting dissolution experiments of cellulose with different operating conditions. The solubility of cellulose was represented in terms of weight percent (wt%). The length of the alkyl chain of cation and types of anion used in IL influenced the solubility of cellulose. For instance, [C_4MIM] cation performed better than [C_6MIM] and [C_8MIM] when the same anion was used. In addition, more cellulose dissolved in $[Cl]^-$ anion compared to $[BF_4]^-$ and $[PF_6]^-$ anions as cellulose did not dissolve in them. Heating samples in microwave oven assisted the dissolution process, and further improved the dissolution rates. The solubility of ILs in organic compounds can also be utilized in specific tasks. 13 ILs based on methylimidazolium and alkyl pyridinium cations, and various types of anions were used for extracting organic compounds from transesterification reaction mixtures [41]. The extraction efficiencies of ILs were tested using vinyl butyrate, 1-butanol, butyl butyrate and butyric acid as compounds to be recovered. IL with higher average distribution ratio was more efficient in extracting organic compounds, which in this case [BMIM][Cl] was the most effective IL for the extraction process. In addition, the capability of a specific IL to separate the target compounds was due to the relationship between the distribution ratio and the hydrophilicity of the compounds. The distribution ratio for the compounds was influenced by the alkyl chain length of the ILs cation.

2.5. Acidity and basicity

The characteristic of ionic liquid as green solvent can be highlighted by its nature of having either acid or base properties, which can be modified by altering the combination of cations and anions in IL. According to Welton [18], the ability of IL to act as proton donator (acid) or proton acceptor (base) influenced the acidity or basicity of an IL. The dissociation constant (pK_a) for the transfer of proton from the donator to the acceptor defined the acidity or basicity of an IL, and probe indicator, such as m-Cresol purple can be used to gain more understanding on the dissociation of IL [42]. Factors that determined the acidity of an IL are the presence of different nitrogen groups [43], the length of hydrocarbon chain [44] and the existence of anion in the IL system [45]. Other than that, the acidity of ILs also depends on the amount of water in IL, where higher water content would decrease the acidity of IL solution [46]. The acidity and basicity of ILs are one of the reasons why they are suitable to be used as catalyst in reactions. The suitability of either acid or base ILs as catalyst depends on the nature of reactants used and operating conditions of processes. There are also protic ionic liquids which can be produced by the equimolar mixing of Brφnsted acid and Brφnsted base [47]. Acid–base neutralization is applied for preparing this type of ILs. Detailed review on acidity and basicity of ionic liquids were previously done by Johnson et al. [48] on Brφnsted acidic ILs, Sereda et al. [49] on Lewis acidic ILs, and Hajipour and Rafiee [50] on basic ILs.

Esterification of benzoic acid by Xing et al. [51] utilized 4 types of Brφnsted-acidic task-specific ionic liquids (TSILs), which were synthesized prior to the esterification reaction. N-propane sulfone pyridinium (PSPy) was combined with four strong acids (HBF_4, H_2SO_4, H_3PO_4 and p-TSA$\cdot H_2O$) to produce TSILs, where all of them were miscible with water and partially immiscible with esters. The esterification of two of those TSILs ([PSPy][BF_4], [PSPy][HSO_4]) produced more than 95% ester yield. The anion with higher Brφnsted acidity resulted in better conversion of benzoic acid and also the immiscibility with ester, which in this case was [PSPy][HSO_4]. Recycled IL can be reused after proper separation method, with no significant change in its catalytic activity after being used four times in the esterification process. Novel Brφnsted ILs act as both solvent and catalyst for the Fischer esterification of acetic acid, metacetonic acid and benzoic acid [52]. Six ILs were synthesized with acyclic trialkanylammonium cation, and H_2SO_4 and H_3PO_4 as anions. These ILs were treated under vacuum for 3 days to confirm that they are stable at high temperatures. [TMPSA][HSO_4] produced more ester yield compared to other ILs, as $[HSO_4]^-$ anion has a higher Brφnsted acidity. The activity of ILs was not only dependent on their anion, but also on the alkyl chain of the cation. The immiscibility of ester product with TSILs shifted the equilibrium of Fischer esterification reaction towards its completion. Recycling of [TMPSA][HSO_4] did not show large drop in the conversion, selectivity and yield of ester.

1-methyl-3-butylimidazolium hydroxide ([BMIM][OH]), a basic ionic liquid, was used as the catalyst and reaction medium for Markovnikov addition of N-heterocycles to vinyl esters [53]. The yield of the product ranges between 73% and 93% under mild reaction conditions. The chain length of vinyl ester affected the yield of the reaction, with the activity decreased when longer chain of vinyl ester was used. They also proposed the mechanism of Markovnikov addition reaction catalyzed by the IL. Yang et al. [54] used several types of Lewis basic ILs as the catalyst in the synthesis of oxazolidinones. The conversion and yield of products obtained were compared for the screening of suitable catalyst for the synthesis. The best catalyst was [C_4DABCO][Br], with the $[Br]^-$ anion showed the highest activity compared to other ILs. The catalyst was further used to observe the effect of CO_2 pressure, reaction temperature and catalyst loading on conversion and yield of oxazolidinones product. The reusability of IL was performed and showed a negligible decrease in catalyst activity even after four subsequent cycles. Aside from being used as catalyst in chemical reaction, basic ILs are also used in compound extraction [55]. Glycerol was added to ILs, producing deep eutectic solvents (DES) that was used to extract glycerol from biodiesel, and the addition of ethanol enhanced the miscibility. The Lewis basic mixtures of salt and glycerol must use a molar ratio of 1:1; otherwise it will influence the effectiveness of the extraction process. During the recovery of IL from glycerol, the addition of co-solvent enhanced the separation of the salt and was more effective compared to crystallization of IL or distillation of the glycerol.

3. Switchable ionic liquids as green solvents

Solvents are used in many industries due to the ability of dissolving other substances to form a solution. One or two reacting components are dissolved in a suitable solvent and the reaction is allowed to take place. They are available in liquid or gas forms, and are vital to many industrial reaction and chemical processes, as they influence reaction rates, chemical equilibria, and heat and mass transfer efficiencies. Solvents are either organic (always contain the carbon element) or inorganic (does not contain carbon element), and are often used as the primary component in cleaning agents, adhesives and coatings. Although solvents are important for wide range of industries, however majority of common solvents are flammable and also pose potential health hazards, especially VOCs. They have low boiling points as a result of their high vapor pressure, and can evaporate at room temperature. Furthermore, exposure to VOCs can cause health effects, depending on the type of VOC, the concentration of VOC and the length of exposure. In the presence of sunlight, VOCs can react with nitrogen oxide and other airborne chemical to produce ozone, which is a primary component of smog [56]. Exposure to smog can cause ill health effects, which are mainly related to respiratory problems.

To solve problems related to the utilization of VOCs in chemical reaction processes, the focus is now shifted towards

using ionic liquids as benign solvents. Replacement of conventional solvents by ionic liquids would prevent the emission of VOCs. This is mainly due to their inherent low volatility, which prevents them from evaporating even at elevated temperature. The credibility of ILs as green solvents are further boosted by other interesting properties as well. These include negligible vapor pressure, higher chemical and thermal stabilities, the ability to create biphasic reaction systems, and also their highly tunable combination of ions. Recycling ILs using proper separation methods is essential as the price of ionic liquids far exceeds the price of conventional solvents. Distillation is one of the common methods for reclaiming ILs, but the process is energy intensive and is difficult to remove solutes with high boiling point. In the case where isolating ILs is unfeasible due to presence of components with high boiling temperature, ILs can be recovered using conventional organic solvents. However, this defies the green aspect of ILs as contamination may occur from the use of organic solvents [57].

Switchable ionic liquids (SILs) are solvents which can be changed to either neutral state or ionic state with the introduction of an external stimulus. It is also known as reversible ionic liquids (RILs) as the ionic solvent can be restored to its original non-ionic state due to the reversibility of the reaction [58]. Carbon dioxide is usually used to transform the molecular liquid (non-ionic form) into ionic liquid, while sparging the ionic liquid with nitrogen or argon reverts back to the non-ionic form [59]. CO_2 is ideal for switching the molecular liquid into its ionic form as it is non-toxic, cheap, benign, and easily removed [60]. SIL can be revered back to the neutral state by bubbling with nitrogen or argon, increasing the temperature or applying vacuum [61]. The switchable characteristic of the reversible ionic liquids allow facile separation, recovery and reuse of these solvents following a chemical synthesis or extraction. This feature comes in handy as the need to remove and replace solvents after each reaction step is eliminated.

3.1. One- and two-component systems

There are two types of SILs, which can be distinguished by the presence of alcohol within the system itself. A two-component system requires the presence of a neutral alcohol in equimolar amount to a neutral molecule containing at least one basic nitrogen compound [58]. Examples of molecular liquid that are usually used for producing SILs are 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU) and 2-butyl-1, 1, 3, 3-tetramethylguanidine (TMBG). Using alcohols with different chain lengths for this type of system can influence the properties of SILs, such as their viscosity, miscibility and molecular states [62]. SILs are solid at room temperature when methanol and ethanol are used, while other higher primary alcohols resulted in viscous liquids of SILs at or near room temperature. In a two-component system, maintaining a 1:1 M stochiometry between alcohol and neutral molecule can be quite difficult. In particular, maintaining an equimolar mixture of molecular liquid and alcohol throughout the process is complicated, especially when low boiling point alcohol is used [58].

A two-component system of SIL faced problem when using alcohol with higher volatility. In order to overcome the difficulty, Anugwom et al. [63] substituted alcohol with glycerol for preparation and characterization of SIL based on DBU, glycerol and acid gases (CO_2, SO_2). Glycerol is a by-product of biodiesel production, and its production capacity is expected to increase with wide-usage of biodiesel as renewable fuel for transportation. In the study, the molar ratio of DBU to glycerol was 3:1. Characterization of the ionic liquid system after the addition of CO_2 shows the presence of glycerol carbonate from the NMR spectra, while protonated form of DBU ($DBUH^+$) was observed from the FTIR spectra. Physical properties of the SILs changed when different acid gases were introduced to the system. SIL produced from CO_2 have lower glass transition temperature and onset decomposition temperature as compared to SIL from SO_2. The difference is related to the strength of acid gas binding. Synthesized SILs were mainly miscible with polar solvents, such as water and methanol. Nile Red dye was used to observe the change in polarity. Color changes occurred when CO_2 was bubbled through the mixture, and also when the mixture was sparged with N_2. Thus, it can be concluded that the polarity of the SILs changed from the molecular form to the ionic form, and vice-versa.

In contrast to its counterpart, a one-component system does not need alcohol, and SILs are prepared by bubbling CO_2 through a primary amine molecular liquid precursor to cause the conversion to ionic liquid. The elimination of the requirement for stoichiometric alcohol makes the one-component system simpler than the two-component system, plus there will be no alcohol lost during the reversal to the neutral molecule [64]. Alcohol loss must be replaced to maintain the stoichiometric ratio to enable successful switch to the ionic form. Besides, the alcohol in the two-component system can lead to transesterification when SIL is used for extraction of lipid [65]. As alcohol, especially methanol is consumed by the transesterification process, the stoichiometric ratio is disrupted and affects the switchability of SIL. Nonetheless, the viscosity for one-component system is higher, which can make the separation of solvent problematic [59].

3.2. Properties of switchable ionic liquids

When an SIL is switched between molecular liquid and ionic liquid, its properties changed too. Among the most discussed property of SIL is related to its polarity. Switchable-polarity solvents (SPS) can switch from low polarity to higher polarity when a trigger is applied [66]. Liquid amine used for this type of solvent must be able to form ionic liquid carbamate salt when exposed to CO_2. Although the potential is very big for mixture of DBU/alcohol as SPS, however it is restricted by its price and relatively high polarity even in its low-polarity form. Phan et al. [66] discovered that secondary amines as the suitable candidate as alternative to DBU as it does not need the presence of alcohol to switch to the ionic form. The polarity of an SIL can be measured by using UV–vis absorption of the Nile Red dye. The change in polarity is confirmed when there is a change between the wavelengths in the spectra as the solvent switch from non-ionic form to ionic form. For a two-component system, the length of the alkyl chain on the alcohol influenced the polarity of both molecular and ionic forms of SIL [58]. On the other hand, the difference in alkyl chain side groups of a single-component SIL influenced the magnitude of polarity change [67].

The viscosity of a solvent is important, as lower viscosity solvent will provide more rapid mass transfer rates, hence enhancing the mass transfer progress. The viscosity of SIL increased when the neutral molecule is exposed to CO_2 and switched to ionic form. On the average, the viscosity increased by a factor of six upon CO_2 binding, but it can be moderated by increasing the temperature [61]. A two-component SIL is advantageous in terms of viscosity as it is lower compared to a one-component system, probably due to an excess of one of the molecular liquids [59]. DBU paired with shorter chain alcohol has lower viscosity, and can extract more hemicelluloses from biomass sample as the mass transfer of fluid may have improved compared DBU with longer alcohol chain [68]. The viscosity of ionic liquid is reduced when CO_2 is removed by either bubbling nitrogen or argon through the liquid, or at elevated temperature.

The switchability of SIL can not only alter its polarity, but also its hydrophilicity. This character can be beneficial for solvent in chemical reaction, especially when removing solvent from a mixture of different miscibility. The idea was first introduced by Phan et al. [65], where the group studied on the effective method to extract soybean oil and the separation afterwards. DBU was used as the solvent due to its hydrophilicity nature in the presence of CO_2. However, problem arises as small percentage of DBU remains in the soy oil layer, and the separation becomes difficult when CO_2 is removed as DBU becomes less hydrophilic. The same group extended their previous work in order to find suitable solvent that can switch its hydrophilicity efficiently. N,N,N′-tributylpentanamidine was successfully used in extracting oil from soybean flakes without the need of distillation for solvent recovery [60]. The oil extraction process is summarized in Fig. 3. A number of amidines and guanidines were screened to choose the solvent with greater hydrophobicity behavior. The identified amidine was then used to extract soybean oil. Addition of water and CO_2 induced separation between hydrophobic and hydrophilic phases, thus oil can be removed. The solvent can later be reused again for another cycle of extraction after removal of water. However, further work is required to identify other solvent that has outstanding switchable polarity as N,N,N′-tributylpentanamidine is not commercially available and very difficult to synthesize [69].

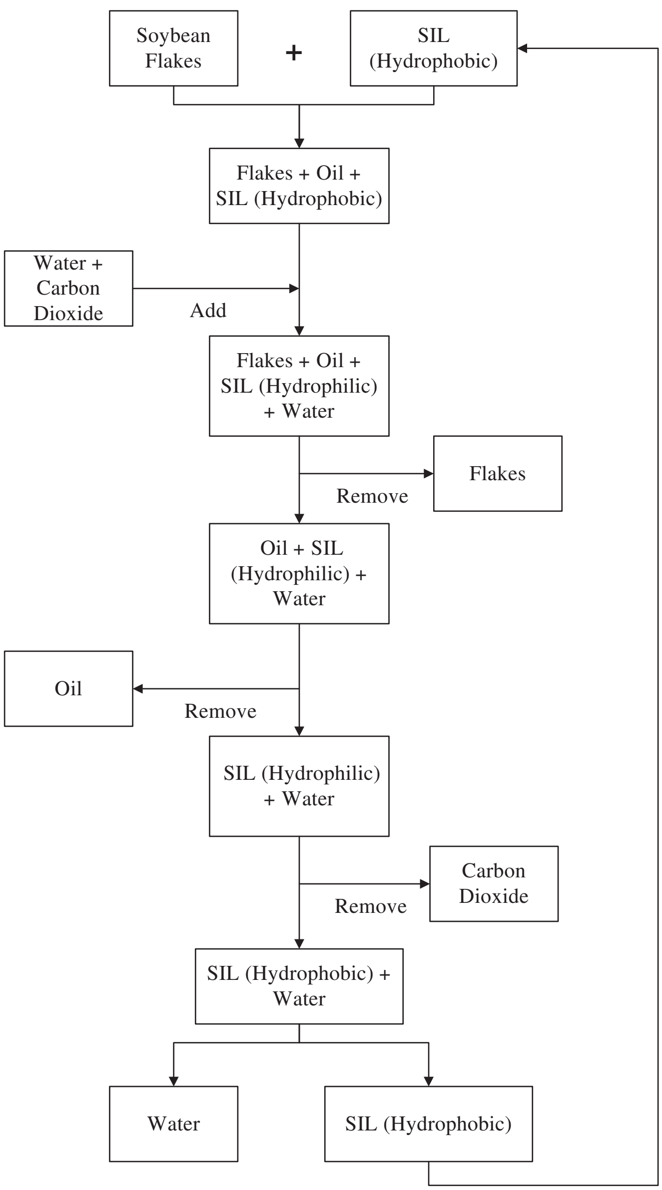


Fig. 3. Flow chart of soybean oil extraction using SIL.

3.3. Switchable ionic liquids application in chemical processes

SILs have been used in different kinds of chemical processes as substitutes to conventional solvents and their application are summed up in Table 1. Up until recently, most SILs are used for CO_2 capture. Even though imidazolium-based ILs have good solubility and selectivity for CO_2, however they are not cost-competitive compared to commonly used chemicals for CO_2 extraction, and also the viscosity is high [70]. Using reversible SILs can overcome the problem faced by conventional ILs. The application of conventional ILs and SILs for CO_2 capture has been discussed thoroughly by Shannon and Bara [71]. Privalova et al. [61] compared the performance of ‘classical’ ILs ([BMIM][BF_4] and [BMIM][Ac]) with DBU-based SIL for capturing CO_2. Amino alcohols were introduced for the two-component SIL system to determine the effect of additional amine group in the process. The inclusion of amino alcohol increased the CO_2 capturing efficiency, and alcohol with longer carbon chain also leads to the same result, although resulted in decreased initial absorption rate. Also, it was proven that [BMIM][BF_4] and [BMIM][Ac] have lower CO_2 capturing efficiency compared to the SIL. Desorption of CO_2 from SIL can be achieved in shorter time with elevated regeneration temperature. Application of ultrasound for the desorption step is feasible and comparable to desorption at degradation temperature of SIL. DBU paired with 4-amino-1-butanol was the most outstanding system based on the CO_2 extraction efficiency and recyclability of SIL.

Blasucci et al. [72] synthesized four SILs from their respective silylated amine precursors for CO_2 capture purpose. They were (3-aminopropyl)-triethoxysilane (TESA), (3-aminopropyl)-trimethoxysilane (TMSA), (3-aminopropyl)-triethylsilane (TEtSA), and (3-aminopropyl)-tripropylsilane (TPSA). Nile red tests showed that solvent polarity increased when they switched into ionic form from their non-ionic precursors. In addition, the longer alkyl chains are less polar in both neutral and ionic forms. The reversal temperatures of SILs differ between 100 °C and 150 °C, as determined by differential scanning calorimetry tests. The highest total CO_2 capacity was achieved by TPSA (20.2 mol CO_2/kg amine), while the lowest was TMSA (13.69 mol CO_2/kg amine). The difference in the CO_2 capacity can be explained by the longer alkyl side groups of TPSA, which enable more efficient CO_2 absorption. Superbase-derive protic ionic liquids (PILs) were materialized for CO_2 capture [73]. These PILs consist of superbases, fluorinated alcohols, imidazole, pyrrolidone and phenol. Majority of PILs synthesized earlier have excellent CO_2 absorption capacity under atmospheric pressure, with the highest being $[MTBDH^{+}]_2[HFPD^{2-}]$. Different proton donors of PILs, gas phase energetics and viscosity influence the absorption of CO_2. The PILs were reversed back to their neutral state simply by heating or bubbling N_2 through the PILs. The second method allows almost complete removal of CO_2 in 10 min.

Aside from capturing CO_2, SILs are also suitable for SO_2 extraction. Wang et al. [74] exploited the reversibility of SIL for enhancing the efficiency of SO_2 capture by azole-based ILs. These ILs were prepared by acid–base neutralization between tetrazole (Tetz) or imidazole (Im) and phosponium hydroxide in ethanol to produce [P_{66614}][Tetz] and [P_{66614}][Im]. The SO_2 absorption capacity increased with the increase of SO_2 partial pressure, but decreased with the temperature. This proved that SO_2 can be desorbed from SILs by heating the system. The anion of SIL influenced the absorption capacity, with [P_{66614}][Im] shows

Table 1
Application of SIL in chemical processes.

Process	SIL system	Molecular liquid	Alcohol	Trigger	Remarks	References
CO_2 capture	Two-components	DBU	1-hexanol, L-prolinol, L-valinol, 4-amino-1-butanol, 6-amino-1-hexanol	CO_2	CO_2 removal efficiency of SIL superior to classical ILs	[61]
Extraction of soybean oil	Two-components	DBU	Ethanol	CO_2	Transesterification of soybean oil occurs due to presence of ethanol	[65]
Extraction of hemicelluloses from spruce	Two-components	DBU	Hexanol, butanol	CO_2, N_2	SIL less effective for lignin removal	[68]
Extraction of hydrocarbon from microalga	Two-components	DBU	Ethanol, octanol	CO_2, N_2	Extraction using SIL better than conventional solvent	[76]
Extraction of soybean oil	One-component	N,N,N′-tributylpentanamidine	–	CO_2	Switchable hydrophilicity facilitates separation of oil from solvent	[69]
Crude oil purification	One-component	TMSA, TESA, TEtSA, TPSA	–	CO_2	Product contaminated by SIL	[72]
CO_2 capture	One-component	TMSA, TESA, TEtSA, TPSA	–	CO_2	CO_2 capture increased with alkyl side groups	[72]
CO_2 capture	One-component	MTBD, P_2.Et	–	CO_2, N_2	Proton donors of SIL influenced CO_2 absorption	[73]
SO_2 capture	One-component	$[P_{66614}]$[Tetz], $[P_{66614}]$[Im]	–	SO_2, N_2	High capacity of SIL for SO_2 removal	[74]
SO_2 capture	One-component	$[P_{444E3}]$[Tetz], $[E_3mim]$[Tetz]	–	SO_2	Ether-functionalized cation improved SO_2 capture efficiency	[75]

incomplete desorption of SO_2 through several cycles. On the other hand, $[P_{66614}]$[Tetz] managed to maintain its SO_2 absorption capacity above 3 mol SO_2/mol IL for 28 cycles. The same group continued to expand their research on SO_2 capture using SIL prepared from ether-functionalized cations and multiple-site tetrazole anions [75]. The synthesized SILs were $[P_{444E3}]$[Tetz] and $[E_3mim]$[Tetz]. The highest SO_2 absorption capacity recorded was 5.0 mol SO_2/mol IL by using $[P_{444E3}]$[Tetz]. Furthermore, only 6 min was required to reach near-completed SO_2 absorption. The presence of ether groups in the cations contributes to this SIL character.

Another application that utilized SILs as solvents is the extraction of hydrocarbon. The capability of SILs to change its polarity upon introduction of CO_2 allows extraction of unwanted hydrocarbon from crude oil, as these non-polar constituents can be separated from oil when the phase separation occurred. Several SILs were derived from siloxylated amines and used for recovery of alkanes from heavy crude oil [67]. 3-(trimethoxysilyl)-propylammonium 3-(trimethoxysilyl)-propylcarbamate (TMSAC) and 3-(triethoxysilyl)propylammonium 3-(triethoxysilyl)propyl-carbamate (TESAC) were prepared and characterized prior to the removal of hydrocarbon. TESAC has lower viscosity and undergoes larger polarity switch, thus is selected for the extraction step. The mixture of oil and the precursor, triethoxysilylpropylamine (TESA) resulted in a single-phase system, and a two-phase mixture appears when CO_2 is bubbled into the mixture. After decantation, the SIL is ready for another cycle of hydrocarbon extraction. The exclusion of heating process for recovering SIL holds the advantage over conventional distillation method, and the separation remains unchanged for three recycles. This method can improved the process economics of hydrocarbon removal from oil.

Samorì et al. [76] reported the extraction of hydrocarbons (i.e. lipids) from *Botryococcus braunii* using a two-component system of SIL. DBU was paired with either ethanol or octanol for the extraction purpose. The process was conducted using freeze-dried microalga sample and also from algal cultures. The equimolar mixture of DBU/octanol resulted in the best yields of hydrocarbons and olefins for both freeze-dried samples and also the algal cultures. This can be explained by the longer carbon chain of octanol; however the alcohol chain length does not influence the rate of extraction. The extraction of hydrocarbon using SILs was even better compared to conventional organic solvent such as n-hexane. There was not much difference in total hydrocarbons extracted when the algal cultures were centrifuged at different speed. The DBU-octyl carbonate salt was reverted to the non-polar state by bubbling N_2. The levels of contamination in oil can be reduced by bubbling extra CO_2 to remove precipitation of ionic liquid from the oil.

The versatility of SILs was further explored by Anugwom et al. [68] for selective extraction of hemicelluloses from spruce. A two-component system was used for the process, with either hexanol or butanol as the alcohol. Previously, conventional ionic liquids have been applied for wood dissolution, but the high viscosity after dissolution hinders effective wood dissolution process. DBU-butanol-CO_2 (SIL_1) and DBU-hexanol-CO_2 (SIL_2) were successfully integrated into the process, with the former achieved higher amount of hemicelluloses reduction than the later. The viscosity of the SILs probably has contributed to this result, where the mass transfer of fluid improved for SIL with lower viscosity. There was not much difference in water content, melting point and decomposition temperature of either SIL. Although the SIL treatment was successful for the extraction of hemicelluloses, the lignin removal was not very successful. An advantage point added to the extraction was it was done at 55 °C and normal pressure, thus minimize energy consumption compared to other existing wood treatment processes. The authors did not conduct the recycling of the SILs in their study, but it will be further explored to justify the greenness of the SILs.

4. Ionic liquids in biodiesel synthesis

The conversion of renewable feedstocks takes place through chemical reaction to produce biodiesel. Conventional organic and inorganic solvents are used in biodiesel synthesis. Although they are usually used due to their wide availability and inexpensiveness, these types of solvents can pose threats on environment,

especially regarding their toxicity and flammability. Furthermore, inappropriate disposal of waste containing these solvents can also lead to contamination of the environment. Ionic liquids offer several advantages over conventional solvents. Their perspective and usefulness in biodiesel synthesis have made their utilization become more prominent. Fig. 4 represents several applications of ionic liquids in biodiesel production.

4.1. Catalyst

There are several types of catalysts that can be used for transesterification process. These include alkaline, acid and enzyme catalysts, with alkaline catalysts are most preferred as the process can proceed at higher reaction rate and available at cheaper price compared to the other two catalysts [77]. While homogeneous catalyst cause difficulties in separation of catalyst from liquid mixtures, severe operating conditions (i.e. reaction time, reaction temperature) are required for producing biodiesel using heterogeneous catalyst. The prospect of ionic liquids as a catalyst in biodiesel synthesis is promising. ILs are considered as homogeneous catalyst because they are in the same phase with reactants, and thus possesses the advantage of homogeneous catalyst over heterogeneous catalyst. In addition, the ability to recycle ILs at the end of reaction and easing the separation of products are benefits obtained if heterogeneous catalyst is used. Hence, by combining these two advantages of homogeneous and heterogeneous catalysts, application of ILs as catalyst in biodiesel synthesis have started to gain popularity. On top of that, advantages in terms of high catalytic activity, excellent stability, easy product isolation and environmental benefits are the reason why ionic liquids are better compared to conventional liquid and solid catalysts [43].

Most of ILs used to produce biodiesel are Brφnsted acidic type ILs [44,78,79]. Other than that, basic ILs [80,81] were also used. Brφnsted acidic ILs are preferred over other basic ILs catalysts because it can be used for transesterification process using feedstock with high free fatty acids content and prevent the problem related to the formation of soap if basic catalysts are used. ILs catalysts used in biodiesel synthesis are listed in Table 2. These catalysts are able to convert different kinds of feedstocks into biodiesel. Moderate reaction temperatures are required to achieve considerably high biodiesel yield. ILs are usually synthesized prior to the biodiesel conversion process and characterized to measure properties required for catalyzing the reaction. The utilization of microwave irradiation allows preparation of ILs to be conducted

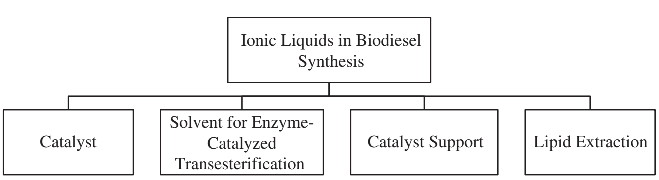


Fig. 4. Applications of ionic liquids in biodiesel synthesis.

in shorter time and in solvent-free conditions, whereas the conventional heating methods are very time consuming and requires relatively high temperature [82]. Among the methods that are used for characterizing ILs are infrared (IR) spectroscopy, nuclear magnetic resonance (NMR), thermogravimetry analysis (TGA) and electrospray ionization mass spectrometry (ESI-MS) [83,84].

IR spectroscopy test utilized the unique molecular properties of a sample. The spectrum representing the molecular absorption and transmission of infrared radiation can be used to identify unknown materials in a sample. Fourier transform infrared (FTIR) method was used by Qureshi et al. [85] to determine the Brφnsted acidity of the synthesized ionic liquid, with pyridine as a probe molecule. The test proved that Brφnsted acid site was present in the tested IL from a band generated in the resulting FTIR spectra, merely due to the formation of pyridinium ions. The FTIR method was applied to evaluate the Lewis acidity of ionic liquids [86]. The probe liquid (pyridine) was mixed with ionic liquid prior to the test. The observed band shifts showed the coordination of pyridine to Lewis acid sites, and concluded that four ionic liquids tested have similar Lewis acid strength as they produced the same band shift of pyridine molecule. NMR spectroscopy test can be employed for determination of ionic liquid structure and also its reactivity. Wu et al. [43] used this method to verify whether the synthesis and purification methods for the ionic liquid produced was adequate, and the absence of impurity peak in the ^{1}H NMR spectra from the NMR spectral data confirmed that the purity of the ionic liquid was more than 95%. Joseph et al. [87] characterized synthesized IL using ^{1}H NMR method, and suggested that the IL might be acidic due to resonation of protons between two nitrogen in the imidazole ring.

TG analysis is used to determine the thermal decomposition temperature of ionic liquid. Higher decomposition temperature is quite useful for an ionic liquid, especially during its purification, which may involve the use of high temperature for the separation of IL from other compounds. Wu et al. [43] discovered that all 5 ILs produced had high decomposition temperature (more than 300 °C). Stefan et al. [88] applied the TG analysis to observe the thermal behavior of ILs by determining the mass losing temperature (T_{ml}) of a series of N-alkyl-N-alkyl′-pyrrolidinium-bis (trifluoromethanesulfonyl) imide (TFSI-) ionic liquids, and the analysis shown that the temperature varies from 305 °C to 321 °C. Other methods that have been used for the characterization of ionic liquid are UV–vis spectroscopy [89,90], which determines the Hammett acidity function of ionic liquid, and also differential scanning calorimetry (DSC) method for thermal analysis measurements [88,90].

One of the earliest study that used ILs for catalyzing biodiesel conversion process was reported by Wu et al. [43]. The transesterification of cottonseed oil into biodiesel was conducted in the presence of Brφnsted acidic ILs as catalysts for the reaction. Prior to the experiment, five ionic liquids were synthesized and later characterized using NMR, FTIR, ESI-MS and TGA analyses. Three different cations were used to produce required ILs, which were

Table 2
Ionic liquids used as catalyst in biodiesel synthesis.

Catalyst	Feedstock	Time (h)	Reaction temperature (°C)	Alcohol to oil molar ratio	Biodiesel yield (%)	References
[BMIM] [CH_3SO_3]–$FeCl_3$	Jatropha oil	5	120	2:1	99.7	[44]
[NMP] [CH_3SO_3]	Oleic acid	8	70	2:1	96.5	[78]
[C_3SO_3HMIM] [HSO_4]	Tung oil	6	150	17:1	97.7	[79]
IMC_2OH	Cottonseed oil	5	60	12:1	98.6%	[80]
[BMIM][OH]	Glycerol triolate	8	120	9:1	87.2	[81]
$ChCl \cdot ZnCl_5 \cdot H_2SO_4$	Palm oil	4	65	15:1	92.0	[93]
[Et_3NH] [Cl]–$AlCl_3$	Soybean oil	9	70	12:1	98.5	[96]

pyridine, N-methylimidazole and triethylamine, each with different Brφnsted acidity strength. All ILs prepared consisted of an alkane sulfonic group within their structure. The highest yield of fatty acid methyl esters was recorded at 92% using 1-(4-sulfonic acid) butylpyridnium hydrogen sulfate as the catalyst. Pyridinium-based IL dissociates H^+ ion easier than imidazolium- and triethylammonium-based IL, which resulted in a stronger Brφnsted acidity. This is supported by the fact that pyridinium-based IL exhibited the best catalytic performance in the experiments conducted. The performance of IL catalyst in transesterification reaction was compared with concentrated sulfuric acid (H_2SO_4) under the same reaction condition. After 3 h have passed, FAME content using IL as the catalyst was 81%, while FAME yield of 86% was produced when using concentrated sulfuric acid. This proved that the catalytic activity of IL was comparable to concentrated H_2SO_4.

Fang et al. [91] conducted esterification of free fatty acids (FFA) into biodiesel using both monocationic and dicationic ionic liquids to compare their catalytic performance for the synthesis of biodiesel. Three dicationic Brφnsted acidic ionic liquids (DAILs) were synthesized prior to the experiment, and later were characterized to determine their melting points, absorption spectra, and also their Hammett acidity. The acyclic ammonium, pyridinium and imidazolium-based acidic ionic liquids were also prepared to represent monocationic ILs. From the Hammett acidity analysis, DAILs acidities increased slightly with an increase of the carbon chain between dications. Their results showed that higher conversions of oleic acid were achieved with the presence of DAILs in the reaction system (95–96% conversion) compared to when monocationic ionic liquids were used (85–87% conversion), proving that the Brφnsted acidic intensity of DAILs was superior to monocationic ILs in terms of catalytic activity. Later, the DAIL with the best catalytic activity ([TMEDAPS][HSO_4]) was used to observe its performance for esterification of other FFAs and short-chain alcohols. From the results, there was no significant difference in conversion of FFAs when the length of the alkyl chains of alcohols and different fatty acids were used. It is proven that [TMEDAPS][HSO_4] can achieve high activity for the conversion of FFAs into biodiesel using different alcohols and FFAs.

A novel ionic liquid with four SO_3H functional groups was used by Liang and Yang [92] as the catalyst for transesterification of rapeseed oil. The novel Brφnsted acidic catalyst has very high acidity and also high polarity due to the presence of multiple functional groups. The high acidity of the catalyst leads to higher catalytic activity for conversion of rapeseed oil into biodiesel, while its high polarity is related to the ease of IL recovery at the end of the reaction. It was synthesized from hexamethylenetetramine and 1,4-butane sulfonate, and then characterized using NMR spectroscopy to check for its purity. The highest biodiesel yield obtained was 98.3% with moderate reaction temperature (70 °C) and 7 h reaction time. A point worth mentioning from the experiment was that the catalyst has good water resistant ability. When the water content was increased 0.3–2.0%, the yield only decreased from 98.3 to 95.3%, indicating that the catalyst is tolerant to water content up until a certain value. Furthermore, the catalytic activity of the novel catalyst was higher compared to those of conventional catalysts, such as sulfuric acid and phosphoric acid. In addition, the quality of purified biodiesel earlier was within the standard of EN 14214.

The inclusion of metal chlorides in ionic liquids increased the conversion rate of free fatty acids and jatropha oil into biodiesel [44]. Seven ionic liquids were used in esterification of oleic acid to screen which IL gave the highest conversion. Bivalent metallic ions (Cu^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}) and trivalent metallic ions (Fe^{3+} and Al^{3+}) were added into [BMIM][CH_3SO_3] to promote the esterification reaction. Reaction conditions, such as temperature and catalyst loading reduced considerably when combining Brφnsted acid of IL and Lewis acids of metal ions. For the transesterification of jatropha oil into biodiesel, only 12% FAME yield was produced when only [BMIM][CH_3SO_3] was used as the catalyst, while the highest FAME yield obtained was 99.7% with the inclusion of Fe^{3+} ions. IL with trivalent metallic ions has higher activities compared to bivalent metallic ions as they are stronger Lewis acids with a larger atomic radius element. Isahak et al. [93] used metal chloride salts for the conversion of palm oil into biodiesel. $ZnCl_5^-$ and $FeCl_7^-$ were utilized to produce choline chloride-metal chloride type ionic liquids. Sulfuric acid was included in their study to increase methyl ester yield as the gain in the absence of sulfuric acid only gave 70.4% and 67.4% methyl ester for choline chloride·$ZnCl_5^-$ and choline chloride·$FeCl_7^-$ catalysts, respectively. Also, biodiesel yield increased as more H_2SO_4 was used. Catalyst deactivation was observed after it has been used for five times, where the yield decreased to 30%.

Although most biodiesel synthesis are conducted using Brφnsted acidic ionic liquids as catalyst, basic ionic liquids can also be used as an alternative to acidic ionic liquids. Liang et al. [80] used basic dicationic ILs as catalysts for the transesterification of cottonseed oil to biodiesel. 5 basic dicationic ILs were prepared by synthesizing imidazolium-based salts of different number of carbon atoms in alkyl-chain with sodium hydroxide (NaOH) and characterized using IT spectra to observe the structures of target ionic liquids. The highest FAME yield was achieved (98.6%) when bis-(3-methyl-1-imidazolium-)-ethylene dihydroxide (IMC_2OH) was used as the catalyst, while all 5 ILs gave selectivity of biodiesel above 99% for the transesterification of cottonseed oil. The optimum temperature for conducting the reaction was 55 °C, which was considered mild condition compared to transesterification using Brφnsted acidic ILs, which sometimes may require up to more than 100 °C to achieve high biodiesel conversion. Basic ILs can be utilized for biodiesel synthesis of cottonseed oil as it has low acid value (0.95 mg KOH/g). Other feedstocks with high acid value may not be able to use basic ILs as the catalyst, unless the acid value is lowered using a two-step transesterification process or using a one step transesterification process with acidic ILs as catalyst.

Esterification of FFA can be conducted using ionic liquid prior to transesterification in a two-step biodiesel production. The efficiency of three Brφnsted acidic imidazolium ILs for esterification of crude palm oil (CPO) was evaluated by Elsheikh et al. [94]. They were 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO_4]), 1-butylimidazolium hydrogen sulfate ([BIM][HSO_4]), and 1-methylimidazolium hydrogen sulfate ([MIM][HSO_4]). The thermal decomposition for all these ILs was higher than 370 °C. Among all the catalysts used, [BMIM][HSO_4] recorded the highest FFA conversion when the catalyst used was 4.4 wt%, compared to the other two catalysts which need higher amount of catalyst loading to achieve moderate FFA conversion. The higher acidity of [BMIM][HSO_4] and the longer side chain of the cation justified its higher catalytic activity effectiveness. By conducting the esterification of CPO at optimum conditions, the FFA conversion reached 91.2% in 2 h of reaction time. The same group continued their study for a two-stage biodiesel production from CPO using IL as catalyst [95]. The acidic ionic liquid, triethylammonium hydrogen sulfate ([Et_3N][HSO_4]) was prepared for the esterification of CPO prior to transesterification using KOH. The optimum IL concentration for the process was found to be 5.2 wt%, and further increased in the amount of IL did not significantly enhanced the FFA conversion. Increased in reaction time, molar ratio of methanol to CPO and reaction temperature also resulted in increased FFA conversion. The resultant biodiesel produced after transesterification step were comparable to international standards of ASTM D6751 and EN 14124.

The combination of cation and anion influence the performance of ionic liquids as catalyst in biodiesel synthesis. Liang et al. [96] produced biodiesel from soybean oil using ionic liquids mixed with metal chloride as a catalyst for the reaction. After $AlCl_3$ was identified as the best metal chloride that gave highest biodiesel yield, the effect of amines that formed the cation of ILs on the reaction was studied. Among ILs that produced yield of biodiesel above 80% were $[Et_3NH][Cl]–AlCl_3$, $[HMIM][Cl]–AlCl_3$, $[C_4MIM][Br]–AlCl_3$ and $[C_{12}MIM][Br]–AlCl_3$. The observed pattern was the catalytic activities decreased with the length of hydrocarbon chain of the amines, probably due to the steric hindrance. Li et al. [97] used pyridinium-based ionic liquids as catalysts in transesterification of Jatropha oil. In the experiments, anion with stronger Brφnsted acidity has higher conversion of biodiesel. For example, the higher acidity of the anion in $[BSPy][CF_3SO_3]$ gave higher FAME yield (83.3%) compared to FAME yield using [BSPy][pTSA] as catalyst (75.5%) even the former reaction was carried out at lower temperature than the latter. Furthermore, the catalyst with higher acidity in anion ($[BSPy][CF_3SO_3]$) has the best immiscibility with the produced esters, as there were only 2.1% of esters presence in the heavy phase of reaction products at the end of the reaction. This indicates that ILs with stronger anion facilitates the shifting of the equilibrium to the product side.

4.2. Solvent for enzyme-catalyzed transesterification

The use of ionic liquids in biocatalysis offers a better alternative to organic solvents, especially biodiesel synthesis using enzyme as catalysts [98–103]. No inactivation of enzymes and increased stability of enzymes in ionic liquids are the reasons for which they are preferable compared to organic solvents for processes involving enzymes in the reaction [104]. Table 3 sums up ionic liquids involved in biodiesel synthesis with enzyme as catalyst. Apart from having lower volatility that prevents vaporization of ILs at room temperature, enzyme can also be recycled when replacing organic solvents with ILs for biodiesel synthesis.

Ha et al. [105] screened 23 ionic liquids as solvent in production of biodiesel from soybean oil using *Candida antarctica* lipase as catalyst. [EMIM][TfO] produced the highest biodiesel yield (80%) in 12 h of reaction. The yield was better than for the solvent free system and other commonly used solvent (*tert*-butanol). Furthermore, the conversion of FAME was better in [EMIM][TfO] as the conversion maintained until 24 h after it reaches its maximum yield, while the conversion of FAME in *tert*-butanol decreased after 12 h. The higher viscosity of [EMIM][TfO] compared to *tert*-butanol leads to lower conversion in the early reaction phase because of the mass transfer limitation.

19 RTILs were studied to determine their effectiveness as solvent in the transesterification process using *Burkholderia cepacia* lipase (BSL) as catalyst [106]. These ionic liquids have different combination of cations and anions, with most of the cations are imidazolium-based. Biodiesel yield increased with cation of longer chain length and increasing hydrophobicity of ILs, and decreased when RTILs with strong water miscible properties are used. Among RTILs tested, $[OmPy][BF_4]$ resulted in highest biodiesel yield after 12 h reaction ($82.2 \pm 1.2\%$), and after 3 cycles, the catalytic activity of the lipase decreased as only 58% yield was detected. Biodiesel yield using $[OmPy][BF_4]$ are higher than other organic solvents, such as n-hexane and tert-butanol, and the application of ultrasound improved transesterification process. The mass transfer limitation due to high RTILs viscosity is decreased, thus allowing the process to proceed faster without compromising biodiesel yield.

Sunitha et al. [107] used four ionic liquids for the conversion of biodiesel from sunflower oil, catalyzed by *Candida antarctica* lipase. Two of them were hydrophobic ILs while the other two were hydrophilic ILs. The reaction in two hydrophobic ILs produced as high as 98% FAME yield for both $[BMIM][PF_6]$ and $[EMIM][PF_6]$. On the other hand, hydrophilic ILs were not suitable as solvent in enzyme-catalyzed transesterification as only 10% FAME yield was obtained for $[HMIM][BF_4]$, while no FAME was observed when $[BMIM][BF_4]$ was used as the solvent. This is explained by the function of hydrophobic IL in protecting lipase from being deactivated by methanol, thus maintaining the catalytic activity of enzyme for transesterification process. The inability of hydrophilic IL to prevent the deactivation of lipase by methanol was justified by the low FAME yield obtained.

Ruzich and Bassi [108] utilized hydrophobic ionic liquid ($[BMIM][PF_6]$) as immobilizing agent for enzyme (lipase) catalyst in production of biodiesel. Rather than using methanol, they chose to use methyl acetate as acyl acceptor for the reaction. This is because methanol and glycerol produced from transesterification process can inhibit lipase and further deactivate the catalyst. $[BMIM][PF_6]$ was used as the immobilizing agent for enzyme as hydrophilic IL caused deactivation of lipase by discarding the water required to maintain lipase's catalytic activity. 80% biodiesel yield was achieved in the presence of ionic liquid when 4 mL of ionic was used in the reaction mixture, which provided larger area of contact between oil and immobilize lipase matrix, thus increased the catalytic activity. In addition, separation of the products becomes easier when using ionic liquid as biphasic system was produced at the end of the reaction, and any unreacted methyl acetate and by-product were in the bottom phase containing ionic liquid. Lipase with ionic liquid can be

Table 3
Ionic liquids used as solvent for enzyme-catalyzed transesterification.

Ionic liquid(s)	Feedstock	Catalyst	Acyl acceptor	References
$[OMIM][PF_6]$, $[TROMA][NTf_2]$, $[C18MIM][NTf_2]$	Triolein	*Candida antarctica* lipase B	Methanol	[98]
$[BMIM][PF_6]$	Corn oil	*Peniclium expansum* lipase, Novozym 435, Lipozyme TLIM	Methanol	[99]
$[BMIM][Tf_2N]$, $[Me(OEt)3\text{-}Et3N][Tf_2N]$, $[Me(OEt)3\text{-}Et\text{-}Im][Tf_2N]$, $[Me\text{-}(OEt)3\text{-}Me\text{-}Et\text{-}Im][Tf_2N]$	Miglyol® oil 812	*Candida antarctica* lipase B	Methanol	[100]
$[BMIM][PF_6]$	Corn oil	*Penicillium expansum* lipase	Methanol	[101]
$[BMIM][PF_6]$	Microalgal oil (*Chlorella pyrenoidosa*)	*Candida antarctica* lipase B, *Penicillium expansum* lipase	Methanol	[102]
$[BMIM][BF_4]$, [EMIM][TFO], $[BMP][BF_4]$, $[BMP][PF_6]$, [BMIM][TFO], $[BMIM][NTf_2]$, $[BDMIM][NTf_2]$, $[EMIM][NTf_2]$, $[OMIM\ NTf_2]$, $[OMIM][PF_6]$	Sunflower oil, waste cooking oil	*Candida antarctica* lipase B	Methanol	[103]
$[BMIM][PF_6]$, $[EMIM][PF_6]$, $[HMIM][BF_4]$, $[BMIM][BF_4]$	Sunflower oil	*Candida antarctica* lipase B	Methanol	[107]
$[BMIM][PF_6]$	Triolein	*Candida antarctica* lipase B	Methyl acetate	[108]
$[C_{16}MIM][NTf_2]$, $[C_{18}MIM][NTf_2]$	Triolein	*Candida antarctica* lipase B	Methanol	[109]

further used in subsequent runs of biodiesel production after separation with the upper layer containing biodiesel without further purification steps.

Two ionic liquids, $[C_{16}MIM][NTf_2]$ and $[C_{18}MIM][NTf_2]$ were used as solvent in for enzyme-catalyzed transesterification of triolein, with *Candida antarctica* lipase B as the catalyst [109]. The yield of FAME using $[C_{16}MIM][NTf_2]$ were maintained around 100% even after 9 days of operation, while the production of FAME for the other IL decreased after the 7th day. The decreased catalytic activity of lipase in $[C_{18}MIM][NTf_2]$ may be contributed by its higher viscosity and the increase in the length of the alkyl chain of the cation. The triphasic system created at the end of transesterification reaction enable easier separation of biodiesel from reaction mixture. Ionic liquid was recovered by solidifying it at the temperature of below 20 °C.

4.3. Catalyst support

Ionic liquids can be used as catalyst support in biodiesel synthesis. Generally, catalyst is attached onto the support, which provides sites for the reaction to occur. The reaction can be increased by using support with high surface area, such as porous materials. The support can either be inert or participate in the catalytic reactions. Among solid catalyst supports previously used in biodiesel production were alumina [110], silica [111] and zeolite [112]. Some support enables the recycling of catalyst, which can be used in subsequent runs.

Abreu et al. [113] compared the effectiveness of ionic liquid and organic solid phase as catalyst support for tin complexes in biodiesel production from vegetable oils. The ionic liquid used was 1-butyl-3-methylimidazolium hexafluorophosphate ($[BMIM][PF_6]$). The anchoring of tin complexes to catalyst supports were carried out prior to the transesterification process. A triphasic system was produced at the end of the reaction of tin complexes in ionic liquid, where the upper layer consists of FAME, the middle layer contains water and hydroxyl compounds, and the bottom layer contained ionic liquid. The catalytic activity of the catalyst dropped drastically after the second recycle, where the yield decreased from 58% to almost no yield after being recycled for two times. The leaching of catalyst from the ionic phase explained the dropped in catalytic activity. Meanwhile, for tin complexes attached to acid resin support, biodiesel yield was very low, probably due to the deactivation of acid sites in both catalyst and its support.

DaSilveira Neto et al. [114] claimed that 1-butyl-3-methylimidazolium tetrachloro-indate ($[BMIM][InCl_4]$) was better than $[BMIM][PF_6]$ as catalyst support in biodiesel synthesis. After catalyst screening, $Sn(pyrone)_2$ was chosen as the catalyst to be supported in ionic liquid. Reaction yield increased during the experiment conducted for 10 h, with a decreased in yield occurred after 4 h due to the reversibility of the reaction. The catalyst with its support was later recycled, and biodiesel yield dropped from 83% yield during the 1st cycle to 3% yield after the 3rd cycle, showing that $[BMIM][InCl_4]$ was better than $[BMIM][PF_6]$ in terms of retaining catalyst in IL. They also showed that transesterification product decreased as the alkyl chain length of alcohol increased; with biodiesel yield using methanol gave the highest yield (83%).

Lapis et al. [115] converted soybean oil into biodiesel using both acid and basic catalysts in ionic liquids as catalyst support. Among seven ionic liquids tested, $[BMIM][NTf_2]$ gave the highest biodiesel conversion (99%) with the shortest reaction time of 0.5 h, using basic catalyst. The decomposition of $[BMIM][BF_4]$ and $[BMIM][PF_6]$ was detected after 2–3 h. The transesterification of soybean oil was also successful when sulfuric acid was used as the catalyst supported by IL. The use of n-butanol and isoamyl alcohol managed to get conversion of biodiesel comparable to the one that uses methanol. The use of Lewis acids for transesterification process also produced 99% yield. However, 13 h of reaction time was required.

4.4. Lipid extraction

Liquid–liquid extraction (LLE) is an important process in analytical chemistry, which involves the separation of the compounds based on their relative solubility. Conventional organic solvents used in LLE process have several disadvantages, such as immiscibility with water, lower boiling point and flash point, and also toxic. The potentials of ILs are thoroughly explored as a replacement for organic solvents in chemical analysis. Other than being typically non-flammable and non-volatile compounds, they also have unique features, such as their polarity and hydrophobicity, which can be altered by changing the nature of the cationic or anion constituents. Lipid extraction is essential for production of biodiesel, especially for microalgae. Oil is commonly obtained from microalgae biomass using Soxhlet extraction with hexane solvent before converting the oil into biodiesel [116]. Other solvents suitable for extracting oil include petroleum ether, ethanol or a hexane–ethanol mixture. However, using ethanol caused extraction of other components that are not desirable for oil extraction purpose, such as sugar, proteins, and pigments [117]. Hence, the ability of ionic liquid as medium for lipid extraction is studied in order to enhance the efficiency of the process.

Young et al. [118] studied the ability of 1-ethyl-3-methyl imidazolium methyl sulfate ($[EMIM][CH_3SO_4]$) to extract lipids from biomass samples. In their research, a mixture of $[EMIM][CH_3SO_4]$ with several types of polar covalent molecule (PCM) was used for extracting lipids from microalgae biomass (*Chlorella sp. and Duniella sp.*), Jatropha oil seed, Kamani oil seed, and Pongamia oil seed. The IL was chosen for their experiment due to its low viscosity, immiscibility with lipids and solubility with selected PCMs. Experimental yields of extracted lipids from different biomass types are within the range from the reported literature values and independent laboratory testing, with the highest experimental yield of lipid was recorded for Jatropha oil seed (49.9% lipid extracted). The dual polarity of IL (hydrophobic and hydrophilic) suggested that lipids can diffuse into IL, thus enabled lipid extraction from the biomass sample. Kim et al. [119] used several ionic liquids to extract lipid from *Chlorella vulgaris* microalga. The effectiveness of ionic liquid to extract lipid was compared with the conventional Bligh and Dyer's method. From the fatty acid composition analysis, $[BMIM][CF_3SO_3]$ extracted the highest amount of total lipids, and even higher compared to the conventional Bligh and Dyer's lipid extraction method. They suggested that anion structure, and the hydrophobicity or hydrophilicity of ILs influenced the extraction efficiency of lipids.

5. Recycling of ionic liquids

Recyclability of ionic liquids is a major factor that can influence its utilization in industries, especially in large scale application. One of the reasons that hindered the application of ILs in a large scale process is due to the prices, which are very costly compared to conventional solvents. This is reflected by the price of ionic liquids that are usually 2–100 times more expensive than the cost of organic solvents [120]. Although the gap in cost of ILs with conventional solvents is very big, an option to offset this drawback is by reclaiming ionic liquids and then recycles them for the next process. By doing this, the disposal of ILs in industrial application can be minimized, thus reducing its impact on the environment. For instance, in biodiesel production process, the catalyst used is discarded after the transesterification step, especially homogeneous

catalyst. Due to the extent of the production scale, catalyst is rarely recycled due to the costs involved. Homogeneous catalyst, such as sodium hydroxide or sulfuric acid is removed from biodiesel by using water washing method during the downstream processing, and the wastewater is hazardous to the environment as it contains traces of organic solvents.

The nature of IL used affected its recycling process. Wu et al. [57] emphasized that the recovery of hydrophilic ILs is more difficult compared to hydrophobic ILs, with the use of membrane technology is an attractive method in separation of ILs as its one of the technology that has already been used at the industrial scale. Hydrophobic ILs are preferred in chemical reaction synthesis, as they can create multiple phase at the end of the reaction. Two phases were formed at the end of biodiesel synthesis conducted by Ruzich and Bassi [108], with biodiesel and other reactants were in their respective layers. The addition of water created another phase between the two phases, allowing easier removal of product. On the other hand, using water-miscible ILs leads to no phase separation and remained in the aqueous phase, thus makes separation more difficult. The addition of potassium salt to hydrophilic ionic liquid can induce the formation of biphasic system, which further assisted the phase separation [121]. Other than that, aqueous biphasic system was formed when sucrose was added into hydrophilic ILs, which enabled recycling of ILs after separation step [122].

5.1. Ionic liquids recovery

Even though IL is considered as homogeneous because it is in the same phase as the reactants, its capability to be recovered and recycled is an advantage over conventional homogeneous solvents. Before ILs can be recycled, they have to be separated from reactants and products. Homogeneous catalytic system is hard to recycle as it lacks of separation method. Several techniques have been applied for reclaiming IL at the end of the reaction. Due to the high thermal stability and negligible vapor pressure, IL can be recovered after removal of volatile components using thermal-based application, such as distillation. In the esterification of aliphatic alcohols with Brφnsted acidic ILs as catalysts, ILs were recovered by applying distillation method to remove methanol and methyl butyrate in the reactant mixture [123]. Here, methanol and methyl butyrate can be removed as they are more volatile and have lower boiling point compared to IL, thus only IL remained in the flask after the separation step. Vacuum distillation and steam distillation methods were utilized in removal of reaction products in Friedel–Crafts benzoylation reaction, where ILs were used as catalyst support [124]. Both methods were successful in separating products from IL-catalyst system, but there was decrease in catalytic activity of the solution after distillation process had been applied.

Recovering ionic liquid using evaporation method is quite unsustainable when the amount of energy required to generate heat is taken into consideration, especially when recovering IL from components with a very high boiling point, of which separation using distillation is not a feasible option. An alternative that does not use high thermal application is by using extraction of IL using carbon dioxide. Blanchard and Brennecke [125] demonstrated the separation of an ionic liquid ([BMIm][PF_6]) from a number of organic compounds using supercritical carbon dioxide ($SCCO_2$) extraction method. The method is effective because organic compounds are soluble in CO_2, while CO_2 and IL are insoluble. This enabled the separation of organic compounds from IL, and depressurization is then applied to remove solutes from CO_2. Furthermore, CO_2 dissolved in the IL phase, while IL is insoluble in CO_2 phase. Scurto et al. [126] studied the separation of IL-water mixture at ambient temperature in the presence of CO_2, with both hydrophobic and hydrophilic IL were used. They discovered that separation of hydrophobic ILs from water was easier compared to hydrophilic ILs, and the separation becomes difficult when there is only small fraction of water in hydrophilic ILs. Increasing the pressure enhanced the solubility of CO_2, but it increased the cost for high pressure requirements.

Another option for IL recovery is membrane separation method. The separation of components in reactant is based on the pore size of the membrane used. The component with larger size than the pore size of the membrane is retained, while the permeate stream contained component that fluxes through the membrane. IL can be separated from solutes using membrane method as long as it has different size and charge from other components. Pervaporation method was used to recover 1-butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF_6] from solutes [127]. The process was successfully conducted at mild operating conditions, with permeates which were free of ionic liquid. The selectivity of the membrane used enables IL to be retained in the system, while other components permeated through the membrane and to the vacuum side. Kröckel and Kragl [128] used nanofiltration (NF) technique to separate hydrophilic ILs from non-volatile products in solutions. ILs can either be permeated or retained in this process, depending on the nature of the membrane used. Multiple filtration steps were required to achieve 93% removal of IL from the system, with the change of IL concentration in the solution reduced gradually during each step. Meanwhile for the retention of IL in the system, the retention value for dicationic IL was higher compared for monocationic IL, indicating that the size of the cation affected the effectiveness of the membrane separation method. Membrane-based processes were used for recycling ionic liquid from water [129]. The separation of IL using nanofiltration and reverse osmosis membranes was influenced by the osmotic pressure of ILs in water. On the other hand, water content in the mixture governed the usability of pervaporation method, where too high water content decreased the flux of water through the membrane.

Recovery of ILs can also be carried out by using crystallization process. Using this method, crystals of ILs are easier to be separated from liquid mixture as they are in different phases (i.e. solid and liquid). The temperature at which IL will solidify is important in this method. In the work by Hayyan et al. [130], 1-butanol was used as anti-solvent for separating choline chloride from glycerin after the transesterification process. After the introduction of the anti-solvent into the extract phase, the temperature was reduced to $-20\,^{\circ}C$, and crystals of choline chloride were produced. Further filtration under vacuum was required to recover IL. Besides, crystallization of IL can also be conducted without the addition of anti-solvent [109]. IL was separated from organic solvent by lowering the temperature of the mixture to under $20\,^{\circ}C$. There are also ionic liquids that have dual heterogeneous and homogeneous characteristics to enhance the separation of catalyst from solvent. Novel Brφnsted acidic ILs based on benzothiazolium cations formed a homogeneous system during the esterification reaction, and then crystallized after the reaction [131]. The catalysts facilitated the separation step as they precipitated after system has been cooled to room temperature.

Physical adsorption is an attractive option for ILs recovery. This is because the simplicity of the operation and the regeneration of the adsorbent reduce the operating cost [132]. Imidazolium-based ionic liquids were separated from aqueous solution using activated carbon (AC) as adsorbent [133]. The efficiency of activated carbon in the adsorption of ILs was evaluated by obtaining the adsorption isotherms of these ILs. From the study, it was determined that the surface chemistry of activated carbon, the size and hydrophobicity for both cations and anions of ILs affected the adsorption capacities. Vijayaraghavan et al. [134] studied the effectiveness of four sorption medias for recovery of

Table 4
Performance of recycled ionic liquids in transesterification and esterification after subsequent runs.

Ionic liquid	Raw material(s)	Number of runs	Initial conversion (C)/yield (Y)	Final conversion (C)/yield (Y)	References
[PSPy][HSO_4]	Benzoic acid	4	88% (Y)	88% (Y)	[51]
[NMP][HSO_4]	Methyl acetoacetate	4	80% (Y)	75% (Y)	[85]
[MIM][BF_4]	Acetic acid	4	90% (Y)	86% (Y)	[87]
[$(CH_2)_4SO_3$HMIM] [CF_3SO_3]	n-butyric acid	4	93% (C)	91% (C)	[123]
[$(CH_2)_4SO_3$HMIM] [HSO_4]	Acetic acid	5	93% (C)	89% (C)	[137]
[NMP][CH_3SO_3]	Acetic acid	6	95% (C)	93% (C)	[39]
[NMP][CH_3SO_3]	Oleic acid	8	95% (C)	91% (C)	[78]
[HMIM][BF_4]	Acetic acid	8	97% (C)	94% (C)	[138]
[HSO_3-pMIM][HSO_4]	Glycerol	10	96% (Y)	92% (Y)	[135]

[BMIM][Cl]. pH condition affected the stability and sorption of the IL. The authors reported that ion exchange resin (Amberlite IRN-150) and activated carbons demonstrated excellent sorption abilities towards [BMIM] cation. On the other hand, bacteria and activated sludge are merely ineffective for the recovery step, probably due to insufficient electrostatic interaction with the IL.

5.2. *Performance of recycled ionic liquids*

The ability to recover and recycle ionic liquid is a positive improvement towards reducing the production cost of a process. Catalytic activity is an important parameter for ionic liquid that is used as catalyst. It is expected that there is insignificant changed in the catalytic activity of recycled IL after proper separation and purification steps. Table 4 summarized the performance of recycled IL in transesterification and esterification processes. There was not much change in catalytic activity of ILs, even after they have been reused for few times. One of the reasons identified for the good reusability of IL is due to the presence of alkyl sulfonic acid group, which maintained the connection to imidazole ring by covalent bonding [135]. In some cases, the recycled IL maintained its catalytic activity after recycling step without significant change in its performance [21,136].

The decline in IL catalytic activity may be caused by deactivation of IL [85], gradual lost of IL during its separation from the reaction product [136], and the presence of unreacted reaction mixture in IL [108]. There was a decrease in the fraction of FAME after basic dicationic IL was used in 7 subsequent runs [80]. The incomplete removal of glycerol and carbonaceous elements attached to the actives sites of the catalyst were the reasons of the declination in catalytic activity. In addition, water content in IL and the acidity of the oil affected the performance of recycled IL as catalyst in biodiesel synthesis from soybean oil [96]. The length of alkyl chains in the cation of IL also influenced biodiesel yield after 9 succeeding cycles, where IL with shorter alkyl chain was better than the longer chain [109].

Other than insignificant decrease in catalyst activity of recycled IL, the selectivity towards product in reactions remains virtually unchanged. Higher selectivity is more favored, as it indicates that more amounts of desired products are obtained, with less formation of undesired products. The role of ionic liquid as catalyst in synthesis of ethyl acetate remained at 100% after recycling steps and used for five cycles [137]. There was no decrease in selectivity to ester in synthesis of butyl acetate, where the selectivity was unchanged (i.e. 100%) even after eight runs after recycling of the IL catalyst [138].

6. Conclusion

The efforts to search for alternative fuels for petroleum-based fuels are becoming more and more extensive in recent years due to limited reserves of crude oil and environmental pollution from petroleum fuel emissions. Biodiesel can be produced from renewable resources and based on the advantages that it possessed, biodiesel fits as a substitute for non-renewable diesel fuel. Transesterification process is widely used in biodiesel synthesis. Organic and inorganic solvents are used in the process to produce biodiesel, but there are some disadvantages related to their characteristics, which may bring harmful consequences to human and environment. Ionic liquids are known as green solvents owing to their properties, and are considered as a suitable replacement for conventional solvents. It has negligible vapor pressure and high thermal stability. In addition several characteristics such as phase transition behavior, soluble and miscible with reactants, and possess acidity and basicity qualify them suitable to be used in biodiesel synthesis. Combination of different cations and anions, the length of alkyl chain of cations, and strong ionic bonds between ions are among the factors influencing the properties of ionic liquids. They can be manipulated to produce task-specific ionic liquids (TSILs) to suit different processes in chemical synthesis.

Ionic liquids can be used as catalyst in transesterification of biodiesel. By having both advantages of homogeneous and heterogeneous catalysts, their utilization as catalyst has a bright prospect. Their catalytic activity is comparable to conventional catalyst. Besides, they are excellent solvents for enzyme-catalyzed transesterification and used as immobilization agent that protected the enzyme from deactivation. Other uses for ionic liquids are as catalyst support that increased the surface area between reactants and catalyst, and also as solvent in lipid extraction from biomass. Although the price for ionic liquids is expensive compared to conventional solvents, the ability to recycle and reused them should be able to offset this drawback. Several methods can be applied to recover ionic liquids from reactants. Further development should be focused on recovering ionic liquids without using extensive energy consumption or potentially hazardous operating conditions. The performance of recycled ionic liquids, especially those that are used as catalyst is impressive. Ionic liquids are able to maintain their catalytic activity based on the yield and selectivity of product after proper separation and purification steps.

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